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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in and relating to the Refining of Metals

We, JOHNSON, MATTHEY & COMPANY LIMITED, a British Company, of 78, Hatton Garden, London, E.C.1, do hereby declare this invention to be described in the following statement:—

This invention relates to improvements in and relating to the refining of metals and more particularly to the purifying of the metals of the A sub-group of the Fifth Group of the Periodic System, namely vanadium, niobium and tantalum, to enable them to be readily worked, such as by rolling and drawing. These metals are rendered brittle and unworkable by the presence of small percentages of nitrogen and oxygen, which hitherto have been found very difficult to remove except by prolonged treatment in a high vacuum at temperatures approaching the melting point of the metal.

Many attempts have been made to produce workable vanadium by reducing the pentoxide or trioxide with metallic calcium, but the product has generally been brittle owing to the presence of up to 0.5% of residual oxygen and/or nitrogen, most of the latter being derived from the nitrogen in the reduction furnace. Vanadium has also been produced by reducing the trichloride with magnesium, but the product of this process is a powder which is rather readily oxidized superficially on contact with the air and, therefore, produces a somewhat hard and brittle ingot on melting in a vacuum furnace; the Vickers pyramid hardness of such ingots is generally in the neighbourhood of 150.

Niobium and tantalum are generally produced by electrolysis or sodium reduction of the double fluoride of the metal and potassium, followed by high vacuum sintering of the cleaned and compressed powder derived from the reduction; the sintered ingot is then further compressed and re-sintered and the product subsequently worked by rolling and drawing. Scrap metal from working opera-

tions is embrittled by heating in hydrogen and broken up into powder which is pressed, degassed by heating *in vacuo*, and then compacted and further treated as for new metal.

It will thus be readily appreciated that none of these three metals is subjected to a melting operation and, therefore, the magnitude of the operation involved in preparing metal for rolling is determined by the equipment available for compacting the powder and heating the compacts in a high vacuum. Furthermore, the time required for, and, therefore, the electrical energy consumed in, carrying out these operations is excessive and considerable advantages in cost of production of ingots and in the recovery of these valuable metals from scrap would accrue if the metals could be melted, refined, and cast into workable ingots in one operation.

We have now found that the above difficulties can be overcome in a simple and practical manner and that the metals in question, namely, vanadium, niobium and tantalum, can be purified and freed especially from nitrogen and oxygen at the same time as they are melted.

According to the invention, a method of refining vanadium, niobium or tantalum, particularly for the removal, or substantial removal, of residual oxygen and/or nitrogen present therein comprises melting the impure metal in an atmosphere or argon in the presence, as purifying agent, of a small quantity of a metal or metal mixture selected from the metals comprised in sub-group A of Group III of the Periodic System as hereinafter defined, said metal or metal mixtures being substantially free from carbon and iron and other metallic impurities.

By the expression "sub-group A of Group III of the Periodic System" is meant the metals scandium and yttrium and the metals of the so-called rare earth group (elements 57—71 inclusive with the exception of ele-

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ment 61, which does not occur in nature).

It is desirable, however, to point out that some of these elements are extremely rare and too costly for use in a commercial process, for example, scandium and the elements of odd atomic number from europium to lutetium inclusive. When the vanadium, niobium or tantalum are to be used for certain purposes in the construction of apparatus for use in nuclear energy work it may be inadvisable to use those elements of Group III which have a high capture cross-section for neutrons, especially samarium, gadolinium and dysprosium.

In carrying out the invention, in practice, although all the individual metals of the rare earth group, as well as yttrium, provided they are substantially free from carbon and iron and other metallic impurities, will be found to be effective purifying agents for the purpose of the invention, we prefer to use pure yttrium, lanthanum or cerium, as we have found these metals to be the most satisfactory on the bases of availability, cost, efficiency and nuclear properties, cerium being the most abundant and the cheapest to produce in a pure form and yttrium the most efficient on a weight basis. If desired, however, a mixture of rare earth metals, such as that known as "Mischmetall" may be used.

Purifying agents suitable for use in carrying out the invention are preferably prepared by reduction of the fluoride or fluorides of the Group III metal or metals with metallic calcium or lithium, as if prepared in the normal manner by electrolysis of the fused chloride or chlorides under commercial conditions they will be found to contain appreciable quantities of carbon and iron and other base metals introduced as impurities from the electrodes or from the containers in which the electrolysis is carried out, which are liable to contaminate the product and would then be quite unsuitable for use in carrying out the invention.

The method of the invention is advantageously carried out in an argon arc melting furnace and we have found that satisfactory results are obtained by the addition of up to 2%, based on weight of the impure metal, of the Group III metal or metal mixture.

When the pure rare earth metal or metal mixture is melted with crude vanadium, niobium, or tantalum containing combined oxygen and/or nitrogen, a slag of oxide and nitride of the rare earth metal or metals is formed which is readily detached from the melted ingot. Any excess of rare earth metal separates as a second layer between the slag and the Group V metal since the solubility of the rare earth metal or metal mixture in the Group V metal is very small (less than 0.2%). This second layer can be removed by mechanical means and used in a further purification operation or it may readily be

dissolved off by treating the ingot with dilute hydrochloric acid. By suitable adjustment of the amount of rare earth metal or metal mixture used in the refining process to the oxygen plus nitrogen content of the Group V metal, it is possible to produce ingots of the latter containing only traces of rare earth metal.

The following examples illustrate the manner in which the invention may be carried out, it being understood that the invention is in no way limited thereto or thereby.

EXAMPLE I.

100 grammes of vanadium produced by reduction of vanadium pentoxide with calcium were found to contain the following impurities: iron 0.1, nitrogen 0.35 and oxygen 0.15 per cent. When melted in an argon arc furnace, it produced an ingot with a Vickers Pyramid Hardness (V.P.H.) of 250. The ingot was very brittle, could readily be broken into coarse crystalline pieces by hammering, and shattered immediately an attempt was made to roll it. The metal was thereupon remelted with 1% of its weight of pure yttrium; the resulting ingot had a V.P.H. of 80 and was readily rolled from 0.5 inch thick to sheet 0.008 inch thick without annealing and could readily be swaged into rod and drawn into thin wire. On analysis it was found to contain iron 0.04%, nitrogen 0.05%, oxygen 0.01% and yttrium 0.15%.

EXAMPLE II.

A quantity of worn tantalum spinnerettes was melted into an ingot and this was used repeatedly as a getter for nitrogen in the purification of commercial argon until it had a V.P.H. of 560 and was so brittle that it shattered on dropping on to a cement floor. This ingot was remelted in an argon arc furnace with the addition of 2% of pure cerium, after which it was coated with a layer of cerium nitride slag below which was a thin film of excess cerium. The slag was detached by hammering and the cerium excess removed by pickling in dilute hydrochloric acid. The resulting ingot of purified tantalum had a V.P.H. of 140 and was readily rolled to thin sheet without annealing; it contained only traces of nitrogen and cerium.

EXAMPLE III.

A quantity of niobium powder produced by reduction of potassium fluoniobate with sodium was compressed into an ingot which was sintered *in vacuo* to remove adsorbed gases and a small carbon content as carbon monoxide and then melted in the argon arc furnace. The ingot had a V.P.H. of 250; it was melted with the addition of 1% of pure lanthanum and then, after cleaning as in Example II, had a V.P.H. of 120 and rolled readily to thin sheet without annealing.

We are aware of Specification No. 773,822, Claim 1 of which claims a method of improving the mechanical properties, particularly the ductility, of metals of Groups IVa, Va, and VIa of the Periodic System and alloys containing more than 50% of such metals, which are contaminated by oxygen and/or nitrogen, which method comprises reacting the molten contaminated metal or the molten alloy with one or more rare earth metals including lanthanum.

The rare earth metals may be used in the form of mixtures or alloys with one another or in the form of alloys with other metals, such as aluminium.

WHAT WE CLAIM IS:—

1. A method of refining vanadium, niobium or tantalum, particularly for the removal or substantial removal of residual oxygen and/or nitrogen present therein which comprises melting the impure metal in an atmosphere of argon in the presence, as purifying agent of a small quantity of a metal or metal mixture selected from the metals comprised in subgroup A of Group III of the Periodic System as hereinbefore defined, said metal or metal mixture being substantially free from carbon and iron and other metal impurities.
2. A method as claimed in Claim 1, wherein up to 2%, based on weight of the impure metal, of the Group III metal or metal mixture is added.
3. A method as claimed in Claim 1 or 2 wherein the metal or metal mixtures purifying agent is prepared by reduction of the fluoride or fluorides of the Group III metal or metals with metallic calcium or lithium.
4. A method as claimed in any of the pre-

ceding claims wherein the purifying agent consists of pure cerium.

5. A method as claimed in any of the preceding Claims 1—3 wherein the purifying agent consists of pure yttrium.

6. A method as claimed in any of Claims 1—3 wherein the purifying agent consists of pure lanthanum.

7. A method as claimed in any of Claims 1—3 wherein the purifying agent consists of pure "Mischmetall".

8. A method as claimed in any of the preceding claims wherein the melting operation is carried out in an argon arc furnace.

9. A method of refining vanadium substantially as described with reference to the foregoing Example I.

10. A method of refining tantalum substantially as described with reference to the foregoing Example II.

11. A method of refining niobium substantially as described with reference to the foregoing Example III.

12. The improved method of refining vanadium, niobium or tantalum substantially as hereinbefore described.

13. Vanadium, niobium, or tantalum whenever refined by the method claimed in Claim 12.

14. Any article or apparatus composed of or containing a part or parts composed of vanadium, niobium or tantalum as claimed in Claim 13.

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Agent for Applicants.

PROVISIONAL SPECIFICATION

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Many attempts have been made to produce workable vanadium by reducing the pentoxide or trioxide with metallic calcium, but

the product has generally been brittle owing to the presence of up to 0.5% of residual oxygen and/or nitrogen, most of the latter being derived from the nitrogen impurity in the calcium or from the atmosphere in the reduction furnace. Vanadium has also been produced by reducing the trichloride with magnesium, but the product of this process is a powder which is rather readily oxidized superficially on contact with the air and, therefore, produces a somewhat hard and brittle ingot on melting in a vacuum furnace; the Vickers pyramid hardness of such ingots is generally in the neighbourhood of 150.

Niobium and tantalum are generally produced by electrolysis or sodium reduction of the double fluoride of the metal and potassium, followed by high vacuum sintering of the cleaned and compressed powder derived from the reduction; the sintered ingot is then further compressed and re-sintered and the product subsequently worked by rolling and

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drawing. Scrap metal from working operations is embrittled by heating in hydrogen and broken up into powder which is pressed, degassed by heating *in vacuo*, and then compacted and further treated as for new metal.

It will thus be readily appreciated that none of these three metals is subjected to a melting operation and, therefore, the magnitude of the operations involved in preparing metal for rolling is determined by the equipment available for compacting the powder and heating the compacts in a high vacuum. Furthermore, the time required for, and, therefore, the electrical energy consumed in, carrying out these operations is excessive and considerable advantages in cost of production of ingots and in the recovery of these valuable metals from scrap would accrue if the metals could be melted, refined, and cast into workable ingots in one operation.

We have now found that the above difficulties can be overcome in a simple and practical manner and that the metals in question, namely, vanadium, niobium and tantalum, can be purified and freed especially from nitrogen and oxygen at the same time as they are melted.

According to the invention, in a method of refining vanadium, niobium and/or tantalum, the melting operation is carried out in an argon arc or similar furnace in the presence of a small quantity of a metal of subgroup A of the III Group of the Periodic System which comprises scandium, yttrium, and the metals of the so-called rare earth group (elements 57—71 inclusive, except 61 which does not occur in nature). It is desirable here to point out that some of these elements are extremely rare and too costly for use in a commercial process, for example, scandium and the elements of odd atomic number from europium to lutetium inclusive. When the vanadium, niobium, or tantalum are to be used for certain purposes in the construction of apparatus for use in nuclear energy work it may be inadvisable to use those elements of the III Group which have a high capture cross-section for neutrons, especially samarium gadolinium and dysprosium. For most purposes, however, the natural mixture of rare earth metals produced by direct reduction of the salt produced in the treatment of rare earth minerals can be used as the refining agent in the process according to this invention. Such a mixture is that known as "Mischmetall", which is obtained by electrolysis of the fused chlorides of the rare earth metals normally found in monazite and obtained as a by-product in the extraction of thorium therefrom.

By suitably modifying the extraction process it is possible to obtain fairly readily a mixture of the so-called light rare earths (lanthanum, cerium, praseodymium, and neodymium) relatively free from those of higher

atomic number and the mixed metal extracted from this oxide mixture forms a satisfactory reducing agent for use in the process according to this invention.

The rare earth metals can be produced from the oxides by a variety of means, for example by electrolysis of the fused chlorides or by reduction of the fluorides with metallic calcium or lithium.

Although all the individual metals of the rare earth group, as well as yttrium, are effective refining agents for vanadium, niobium and tantalum, we have found that the most satisfactory on the bases of availability, cost, efficiency, and nuclear properties are yttrium, lanthanum and cerium. Of these cerium is the most abundant and the cheapest to produce in a pure form, while yttrium is the most efficient on a weight basis.

When the rare earth metal is melted with crude vanadium, niobium, or tantalum containing combined nitrogen and/or oxygen, a slag or nitride and oxide of the rare earth metal is formed which is readily detached from the melted ingot. Any excess of rare earth metal separates as a second layer between the slag and the Group V metal since the solubility of the rare earth metal in the Group V metal is very small (less than 0.2%). This second layer can be removed by mechanical means and used in a further purification operation or it may readily be dissolved off by treating the ingot with dilute hydrochloric acid. By suitable adjustment of the amount of rare earth metal used in the refining process to the oxygen plus nitrogen content of the Group V metal, it is possible to produce ingots of the latter containing only traces of rare earth metal.

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